Solute Absorption into Molten Polystyrene

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Synopsis

The equilibrium volatilities at near infinite dilution of various solutes absorbed in molten polystyrene have been determined by a gas chromatographic technique. This method is much more rapid, although, with the present apparatus, probably less accurate than conventional static techniques. The primary parameters obtained from measurements of retention volumes are the Henry's law constants, from which are derived the weight and volume fraction activity coefficients, the Flory-Huggins interaction parameters, and the heats of dilution and solution.

Of the solutes investigated, 2-butanone (MEK) was the least, and benzene the most compatible (highest and lowest volume fraction activity coefficients, respectively) with molten polystyrene. A small, but definite, variation of the activity coefficients with polystyrene molecular weight was observed.

Introduction

This investigation was prompted by the general lack of reported data on the equilibrium vapor pressure of trace amounts of volatiles over molten polymers. The classic technique for obtaining such data involves the use of a microbalance to measure the gain in weight of a polymer sample in a controlled atmosphere of the volatile component. The GC technique is basically a dynamic *P-V-T* measurement, where the thermodynamic variables may be related to GC parameters such as retention volumes, flow rates, and detector response. Although the former technique is presumably more accurate, the latter was chosen because of its speed and convenience.

The use of polymeric liquid phases in gas–liquid chromatography was firmly established in the late 1950's in order to provide a stationary phase of limited volatility. Few studies, however, were directly devoted to the study of polymer–solute interactions, perhaps due to the lack of physical and chemical data on these ill-defined macromolecular solvents. Recently, there has been a concerted effort to apply gas chromatography to the physicochemical study of polymer–solvent interactions. These have ranged from the purely analytical studies of Bender and Meloan[1] to the assessment

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of χ parameters by Takamizawa and coworkers.[2] In addition to these studies, the recent and extensive work of Guillet et al.[3,4] has established the importance of gas–liquid chromatography as a tool in the study of polymers.

At the present time, the technique is confined to the near infinite dilution region (<0.1 wt-% solute), where the following assumptions usually apply: (1) the ideal gas law is valid for the vapor phase; (2) absorption equilibrium is rapid; (3) the absorption isotherm is linear. Under these conditions, a basic relationship which may be derived (see Appendix) for reduction of the GC data to a physically meaningful parameter is given by eq. (1):

$$\gamma_w = RT/V_g P^\circ M_s \tag{1}$$

where γ_w is the weight fraction activity coefficient, V_g is specific retention volume, P° denotes vapor pressure of pure solute at temperature T, and M_s is the molecular weight of solute. The weight fraction activity coefficient is defined in the usual way, via eq (2):

$$p = P^\circ \gamma_w W \tag{2}$$

where p is the partial pressure of solute and W is the weight fraction of solute. This, of course, is a form of Henry's law for dilute solutions ($P^\circ \gamma_w$ being the corresponding Henry's law constant) using weight fraction as the concentration unit. The use of weight fraction circumvents the intractable question of polymer molecular weight and is simply related to the theoretically more meaningful volume fraction activity coefficient, since:

$$\gamma_\phi/\gamma_w = \rho_s/\rho_p \tag{3}$$

where γ_ϕ is the volume fraction activity coefficient, and ρ_s and ρ_p are the density of solute and density of polymer, respectively, assuming, of course, additivity of volumes on mixing.

The mole fraction activity coefficient has been used by Smidsrød and Guillet,[3] employing an equation analogous to eq. (1),

$$\gamma_x = RT/V_g P^\circ \bar{M}_n \tag{4}$$

where γ_x is the mole fraction activity coefficient and $\bar{M}_n$ is the number-average molecular weight of polymer. Although the use of $\bar{M}_n$ as assumed by the authors is strictly correct (rather than $\bar{M}_w$) for the case at hand—a monodisperse polymer as stationary phase—the mole fraction activity coefficient is meaningless in polymer–solvent solution theory.

To illustrate the major advantage of speed and versatility of the GC technique, various model compounds, including alkylated and chlorinated aromatics, and other solutes, were studied. Inspection of the results may give insight into the nature of solute–polymer interactions and perhaps provide a data base which may become useful in the future. The molecular weight of the polystyrenes used was varied to assess properly the effect of that parameter.

Experimental

The polystyrenes employed in this study were obtained from Pressure Chemical Company, Pittsburgh, Pa., and Arro Laboratories, Joliet, Illinois. These particular polymers were of low polydispersity and were polymerized according to the techniques developed by Altares[5] and Wyman.[6] Additional molecular characterization data have been provided in Table I.

Solutes were obtained from reputable sources and upon chromatography under a multitude of experimental conditions showed no discernible impurities. The support upon which the polystyrene was coated was Chromasorb P, a product of Johns-Manville Corporation, having a mesh range of 80/100. Coating solutions of polystyrene were prepared by dissolving the polystyrene with gentle heating in Baker analyzed reagent grade benzene.

The support has a surface area of about 4m²/g, so that, assuming a uniform coating with polymer, the coating thickness should be at least 0.025 μ. On the other hand, if we assume that the polymer coating doesn't penetrate at all into the pores of the support, and that the support particles are spherical the maximum coating thickness would be about 5 μ. Presumably, the true average thickness lies betweeen these limits and, if so, should be thin

TABLE I
Physical and Chemical Properties of the Polystyrenes Used

	Molecular weight (nominal)			
	3,600	97,200	1,800,000	"Crystal"
$\bar{M}_w$		97,600[a]	2,145,000[b]	200,000[b]
$\bar{M}_n$	3,524 ± 2%[c]	96,200[d]	1,780,000[b]	80,000[b]
$\bar{M}_w/\bar{M}_n$	1.10	1.06	1.205[b]	2.5[b]
$\bar{M}_v$	3,600	98,200 ± 3%[e]	1,890,000[b]	
$\bar{M}_w$ (frac.)			1,906,000[f]	
$\bar{M}_n$ (frac.)			1,607,000[f]	
$\bar{M}_w/\bar{M}_n$ (frac.)			1.86[f]	
Crystallinity (X-Ray)		Amorphous	Amorphous	
Volatiles (H₂O), wt-%		1.0	1.0	
Infrared analysis	No chemically bound impurities	No chemically bound impurities	No chemically bound impurities	
Residue, wt-%[g]		0.01	0.02	
Source	Arro Labs	Pressure Chemical	Arro Labs	Union Carbide Corporation

[a] Light-scattering photometry.

[b] GPC with THF as mobile phase at 25°C.

[c] Vapor-pressure osmometry.

[d] Osmometry (not specified).

[e] Viscometric measurement at Θ conditions (cyclohexane, 34.5°C) and on extrapolating to zero concentration.

[f] Precipitant, methanol at 30°C.

[g] TGA analysis.

TABLE II
Polystyrene Coating Analysis

	Molecular weight (nominal)			
	3,600	97,200	1,800,000	"Crystal"
Coating, wt/wt-%[a]	15.04	10.53	12.51	15.16
Ash analysis, %[b]	86.85	90.37	85.34	—
Weight of polymer on support, g	1.2855	0.9253	1.6142	1.528

[a] Weight of solvent based on weight of support.
[b] Per cent by weight of initial ash mixture (polymer + support).

enough to assure equilibrium with solute vapor but thick enough to avoid adsorption effects.

After coating was accomplished, the coated support was removed carefully and weighed in a stoppered bottle. The approximate amount of polystyrene deposited on the supports is listed in Table II. At the completion of the experiment, the column contents (Chromasorb and polymer) were removed and submitted for ash analysis. The results of the gravimetric ash analysis (Table II) allowed the computation of the weight of the solvent (liquid phase).

The column was $1/4$ in. od copper tubing of 1 m length. Glass wool plugs were used to contain the column packing, which was placed into the tube by a gentle tapping procedure. The column ends were capped until actual installation into the gas chromatograph.

Helium was employed as a carrier gas. In order to minimize pressure drop complications in the column, the ratio of inlet to outlet pressure was kept close to unity. A U-tube manometer was filled with mercury and connected to the carrier gas line in front of the injection port for measuring the inlet pressure.

The commercial gas chromatograph employed with the above described modifications was a Microtek GC 2500R, equipped with a thermal conductivity detector. Flow rates were measured with a soap bubble flow meter. Elution profiles were recorded by using a Honeywell Electronik 19 chart recorder.

Oven temperature measurement was accomplished by using a Hewlett-Packard Model HP-2801A quartz thermometer with sampling every 2.4 sec. The two temperature-sensing probes were placed randomly in the oven volume occupied by the column. Room temperature was measured by using a United States Bureau of Standards Certified Thermometer, No. D-12050.

Simple checks on the dependence of solute retention on sample size produced no noticeable variation in retention volume, and the elution profiles were symmetric, which supports the assumption of equilibrium. A Hamilton 10 μl capacity syringe was used for injection of the solutes into the gas flow. Analysis of each solute was done in triplicate by employing 1.0 μl sample sizes.

The reduction of measured retention time to specific retention volume is amply illustrated in several key texts[7,8] and will not be discussed here. All saturated vapor pressures were obtained from Dreisbach[9] or from internal sources.[10]

Densities for the solutes were obtained directly from data tabulated in Timmermans' compilation[11] of physicochemical constants. Although the highest temperature used in this study (210°C) was considered to be far enough removed from the lowest critical temperature (263°C for MEK) to justify density extrapolation from data at lower temperatures, the theoretical basis for using densities (rather than partial molar volumes) is insufficient to warrant their use. Therefore, since partial molar volumes are not in general known for the cases at hand, the room temperature (25°C) densities were used in converting weight fraction activity coefficients to volume fraction activity coefficients [eq. (3)]. In any case, the density ratio, as required in eq. (3), should be a less pronounced function of temperature than the densities themselves.

Density data for polystyrene exist in the literature[12,13] and are also available as a function of molecular weight.[14-16] The value for "crystal" polystyrene was taken as 1.04 g/cc from internal sources.

Results

The pertinent physical and chemical properties of the polystyrenes used are reported in Table I. The analyses of the amount of polymer on the support are tabulated in Table II. Density data and critical temperatures for the various solutes are listed for convenience in Table III.

The results of the present study on "crystal" polystyrene, in terms of Henry's law constants, weight and volume fraction activity coefficients, and χ parameters, are reported in Table IV. The heats of dilution and

TABLE III
Solute Properties[a]

Solute	Density (25°C), g/cc	Critical temperature, °C
Benzene	0.874	289
Toluene	0.863	320
Ethylbenzene	0.861	344
o-Xylene	0.876	358
m-Xylene	0.860	344
p-Xylene	0.857	343
Styrene	0.906	373
o-Dichlorobenzene	1.303	412
Methyl ethyl ketone	0.800	263
Carbon tetrachloride	1.584	283
p-Dioxane	1.028	315
Chlorobenzene	1.101	359
n-Propylbenzene	0.858	365

[a] Values taken or extrapolated from the literature.[11]

TABLE IV
Limiting Volatility Data for Polystyrene[a]

Temp, °C	1/Temp. (K)	T_o, °C	Solute	P^0, mm Hg	VFAC	WFAC	K	χ
133.32	0.246E-02	289	Benzene	3092.23	3.751	4.463	0.138E 05	0.322
		320	Toluene	1400.08	3.757	4.528	0.633E 04	0.324
		344	Ethylbenzene	722.11	4.036	4.875	0.352E 04	0.395
		358	o-Xylene	560.31	3.954	4.695	0.263E 04	0.375
		373	Styrene	547.92	3.433	4.524	0.247E 04	0.233
		412	o-Dichlorobenzene	201.17	4.896	3.119	0.627E 03	0.588
		263	Methyl ethyl ketone	3331.62	6.023	7.830	0.260E 05	0.796
		283	Carbon tetrachloride	3372.20	4.421	2.903	0.978E 04	0.486
		315	p-Dioxane	1818.83	4.555	4.608	0.838E 04	0.516
171.23	0.225E-02		Benzene	6701.50	3.423	4.120	0.276E 05	0.231
			Toluene	3328.53	3.620	4.362	0.145E 05	0.286
			Ethylbenzene	1854.82	3.738	4.515	0.837E 04	0.319
			o-Xylene	1482.49	3.626	4.305	0.638E 04	0.288
			Styrene	1454.74	3.610	4.144	0.602E 04	0.284
			o-Dichlorobenzene	599.93	3.850	3.073	0.184E 04	0.348
			Methyl ethyl ketone	7450.21	5.308	6.901	0.514E 05	0.669
			Carbon tetrachloride	7218.36	3.690	2.423	0.174E 05	0.306
			p-Dioxane	4278.45	4.158	4.207	0.180E 05	0.425
210.48	0.206E-02		Benzene	12972.51	3.306	3.934	0.510E 05	0.196
			Toluene	6973.21	3.365	4.055	0.282E 05	0.213
			Ethylbenzene	4151.22	3.426	4.138	0.171E 05	0.231
			o-Xylene	3402.90	3.506	4.162	0.141E 05	0.254
			Styrene	3349.12	3.422	3.928	0.131E 05	0.230
			o-Dichlorobenzene	1525.25	3.680	2.937	0.448E 04	0.303
			Carbon tetrachloride	13826.13	3.294	2.163	0.299E 05	0.192
			p-Dioxane	8882.50	4.000	4.047	0.359E 05	0.386

[a] P^0 = Saturated vapor pressure calculated from Antoine equation; VFAC = Volume fraction coefficient; WFAC = Weight fraction activity coefficient $[P = (WFAC)^*(P^0)^*(WF)]$; K = Slope of the isotherm in mm Hg/WF; χ = Flory-Huggins interaction parameters.

TABLE V
Heats of Dilution and Solution in Molten Polystyrene

Solute	ΔH_D, kcal/mole	ΔH_S, kcal/mole
o-Dichlorobenzene	0.30 ± 0.10^a	-9.96 ± 0.20
Toluene	0.55 ± 0.13	-7.58 ± 0.18
o-Xylene	0.61 ± 0.13	-8.52 ± 0.13
Benzene	0.64 ± 0.07	-6.62 ± 0.11
p-Dioxane	0.66 ± 0.13	-7.37 ± 0.12
Styrene	0.72 ± 0.07	8.45 ± 0.10
Ethylbenzene	0.83 ± 0.06	-8.03 ± 0.13
Methyl ethyl ketone	1.20^b	-6.42^b
Carbon tetrachloride	1.49 ± 0.14	-5.65 ± 0.11

[a] Estimated standard deviation about the mean.
[b] Only 2 points, therefore no estimate of error was made.

solution were calculated from the data of Table IV and are listed in Table V. Weight fraction activity coefficients for the various monodisperse polystyrenes studied are reported in Table VI.

The Henry's law constant K is simply $P°\gamma_w$, as mentioned in the introduction. The weight fraction activity coefficients were calculated from eq. (1), and volume fraction activity coefficients from eq. (3). The χ parameter was calculated by use of eq. (5)

$$\chi = (\ln \gamma_\phi) - 1 \qquad (5)$$

which was derived from the results of Flory's theoretical treatment of polymer–solute interactions.[17]

The heat of dilution ΔH_D (also referred to as the excess heat of solution) was calculated from eq. (6)

$$\Delta H_D = R\,d(\ln \gamma_w)/d(1/T) \qquad (6)$$

and represents the enthalpy change associated with the transference of one mole of pure solute liquid into infinitely dilute solution in the molten polymer.

The heat of solution ΔH_S was calculated from:

$$\Delta H_S = R\,d(\ln K)/d(1/T) \qquad (7)$$

and represents the enthalpy change associated with the transference of one mole of pure solute vapor at one atmosphere into infinitely dilute solution in the molten polymer.

The two enthalpies are simply related to the heat of vaporization, ΔH_V, of the soute by:

$$\Delta H_D - \Delta H_S = \Delta H_V \qquad (8)$$

Although the precisions (standard deviations of the slopes of $\ln \gamma_w$ and $\ln K$ vs. $1/T$) of these enthalpies (Table V) appear to be of the order of 0.2 kcal/mole or less, the accuracy of the technique is probably no better than 0.5 kcal/mole, as judged from consideration of the various factors which

TABLE VI
Weight Fraction Activity Coefficients for Solutes over Molten Polystyrene

	Temperature, °C								
	124[a]			148[b]			173[c]		
Solute	$\bar{M}_n =$ 3,600	$\bar{M}_n =$ 96,200	$\bar{M}_n =$ 1,780,000	$\bar{M}_n =$ 3,600	$\bar{M}_n =$ 96,200	$\bar{M}_n =$ 1,780,000	$\bar{M}_n =$ 3,600	$\bar{M}_n =$ 96,200	$\bar{M}_n =$ 1,780,000
Carbon tetrachloride	2.39	3.12	3.76	2.26	2.79	2.98	2.12	2.37	2.59
o-Dichlorobenzene	2.88	3.10	3.66	2.87	3.11	3.37	2.69	2.93	3.22
Chlorobenzene	3.13	3.34	4.14	2.96	3.38	3.70	2.88	3.11	3.36
o-Xylene	3.70	4.74	5.53	3.84	4.42	4.94	3.71	4.15	4.47
Styrene	3.86	4.08	4.95	3.66	4.16	4.51	3.51	3.98	4.20
Benzene	3.93	4.43	5.33	3.80	4.27	4.86	3.67	3.98	4.26
Toluene	3.93	4.52	5.50	3.96	4.43	4.95	3.72	4.24	4.56
Ethylbenzene	3.95	4.61	5.62	3.97	4.51	5.00	3.72	4.31	4.76
1,4-Dioxane	3.97	4.56	5.20	3.95	4.33	4.64	3.71	4.15	4.30
m-Xylene	4.00	4.83	5.98	3.95	4.70	5.22	3.87	4.40	4.63
p-Xylene	4.17	4.68	5.11	3.93	4.55	5.16	3.88	4.44	4.82
n-Propylbenzene	4.28	4.98	6.49	4.20	4.85	5.47	4.12	4.76	4.83
2-Butanone	6.86	7.61	8.72	6.46	7.13	7.64	6.20	6.48	6.88

[a,b,c] The exact temperatures used, for 3,600, 96,200, 1,780,000 MW polystyrene, respectively, were: (a) 126.8, 123.3, 122.3°C; (b) 148.4, 146.8, 147.7°C; (c) 171.6, 174.3, 172.7°C.

enter into the experimental parameters and the reproducibility of the individual measurements, particularly with respect to column-to-column variations.

Discussion

The results for styrene (Tables IV–VI) can be fairly clearly interpreted, at least qualitatively. The weight fraction activity coefficients are not strong functions of temperature, and therefore give a small value for the heat of dilution. This is not surprising since no great differences would be expected to exist in interactions between styrene molecules in an environment of pure styrene and styrene molecules in an environment of polystyrene.

There is also a shallow but definite dependence on molecular weight, as is to be expected since the solute molecule "sees" only a short segment of the polymer molecule. The effect is similar to that observed for poly(ethylene glycols)[18] where V_g changes by $\sim 15\%$ in going from 1000 to 20,000 in molecular weight, and the major change occurs in the low molecular weight region.

Unfortunately, the accuracy of the activity coefficients obtained by the GC method cannot be assessed directly since the appropriate data for polystyrene are not available from literature sources. Data by Kargin[19] for hydrocarbon sorption on glassy polystyrene shows limiting slopes of the isotherms which agree qualitatively with the increase in γ_w with temperature. Our precision is about 3%, and we believe the accuracy should be not more than perhaps 5%.

One direct comparison was found in the literature. Use of an extrapolated value for χ_1 of 0.26 from Bawn et al.[20] for toluene in polystyrene results in a value of 3.56 for γ_ϕ. Our data for toluene at 123°C ($\gamma_w = 4.52$ for polystyrene of 96,000 MW) combined with density data (0.906 g/c for styrene, 1.04 g/cc for polystyrene) give a value of 3.76 for γ_ϕ, a surprisingly close agreement considering the crudeness of the theory.

Inspection of the data for the various solutes over "crystal" polystyrene (Table IV) reveals that methyl ethyl ketone has the largest volume fraction activity coefficient, i.e., is at least compatible with the polystyrene environment, probably due to its being the most polar solute employed. Benzene, on the other hand, has the lowest volume fraction activity coefficient, i.e., is the most compatible with molten polystyrenes, which may be due to favorable π-interactions, and also possibly due to its small molecular size, enabling it to fit into the polymer matrix the most easily.

It should be noted that calculation of partial pressures of styrene and other solutes included in this study, over molten polystyrene, by use of the Henry's law equation, for example, is valid only to the extent that the absorption isotherm in linear up to the region of interest. The GC technique and theory, as employed at present are strictly valid only in the near infinite dilution region, which we estimate to be less than about 0.1 wt-%, typical for normal chromatographic conditions, and therefore extrapolation

beyond this range should be subject to caution. Some confidence in the assumption of isotherm linearity can be provided by visual inspection of the chromatograms, which appear symmetrical over the range of solute amounts covered in this report. Isotherm nonlinearity has been observed[21] even at low concentrations for polar solutes over hydrophobic macromolecules. Additional evidence for isotherm nonlinearity in solute–polymer absorption at the concentration extremes may be seen in the data of Jenckel.[22] Isotherm nonlinearity usually manifests itself in peak skewness, proper analysis of which can lead directly to the sorption isotherm.

APPENDIX

The mole fraction activity coefficient at infinite dilution for the solute is given by the standard expression:[3]

$$\gamma_x^\infty = RT/V_g P^\circ M_P \tag{9}$$

Since the activity coefficients are defined by the expressions (10)

$$p/P^\circ \equiv \gamma_x X_s$$

$$p/P^\circ \equiv \gamma_w W_s \tag{10}$$

the activity coefficients are interconverted by eq. (11).

$$\gamma_x = \gamma_w\, W_s/X_s \tag{11}$$

At near infinite dilution, the weight and mole fractions of solute may be expressed as:

$$W_s \cong \frac{w_P}{w_s} \tag{12}$$

$$X_s \cong \frac{n_s}{n_P} = (w_s/M_s)\,(M_P/w_P)$$

or

$$W_s/X_s \cong M_s/M_P \tag{13}$$

Substituting into eq. (11) gives:

$$\gamma_x^\infty = \gamma_w^\infty\,(M_s/M_P)$$

$$= RT/V_g P^\circ M_P \tag{14}$$

or

$$\gamma_w^\infty = RT/V_g P^\circ M_s \tag{15}$$

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